PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **3** No 1, 01PCSI15(4pp) (2014)

Intrinsic Stress Formation at Plasma-Ion Deposition of TiN Coatings in Pulse Potential Mode

A.I. Kalinichenko, S.A. Kozionov, S.S. Perepelkin, V.E. Strel'nitskij

National Science Center "Kharkov Institute of Physics and Technology", 1, Akademicheskaya, Str., 61108 Kharkov, Ukraine

(Received 31 July 2014; published online 29 August 2014)

Formula for intrinsic stress calculation in coatings deposited from ion flux in the pulse potential mode is derived. The case of deposition of ions with different charges is taken into account. The criterion of applicability of derived formula is proposed which permits determining critical parameters of the pulse potential mode. Calculation of stress in TiN coatings at deposition of low-energy ions Ti^+ from filtered vacuum arc plasma is brought. The qualitative agreement of calculated stresses with experimental data is stated. The important role of deposition temperature for intrinsic stress control in deposited coating is noted.

Keywords: TiN coating, Plasma-based ion deposition, Pulse potential mode deposition, Intrinsic stress, Non-local thermoelastic peak of ion.

PACS numbers: 52.77.Dq, 81.15.Jj

1. INTRODUCTION

Intrinsic stresses σ, arising in coatings at deposition of ion flux substantially determine operational characteristics of obtained coatings. The simple formula for σ calculation was proposed in [1]:

$$\sigma(E,u) \sim \frac{E_Y}{1-\Pi} \cdot \frac{\sqrt{E}}{\xi + w_0(E,u)}, \qquad (1)$$

where E is the ion energy, u is the activation energy of defect migration, E_Y and Π are the Young's modulus and the Poisson's ratio of a target material, ξ is the ratio of fluxes of deposited atoms R and ions j. The number of thermoactivated transitions $w_0(E, u)$ caused by ion was calculated in the model of pointed thermal peak (PTP):

$$w_0(E,u) \approx 0{,}016\left(\frac{E}{u}\right)^{\frac{5}{3}}, \qquad (2)$$

However, the use of the PTP model for description of stress relaxation contradicts to nonlocality of energy transition from ion to matter therefore it is inconsistent. Hereupon analytical curve fits experimental data at values of u = 3 – 11 eV, that multiply exceeds known values of activation energy of defect migration. Therefore, u is mere adjustable parameter in the Davis model [1] excluding its physical interpretation. Also, one should note inherent inconsistency of the model which is developed only for the case of zero temperature of target and for constant thermal capacity at the same time. The last condition contradicts to the Debye theory as experimental data. Hence, this model can not explain experimentally observed dependence of intrinsic stress on deposition temperature.

The following modification of expression (1) was proposed in [2]:

$$\sigma(E,u) \sim \frac{E_Y}{1-\Pi} \cdot \frac{\sqrt{E}}{\xi + w(E,u)}. \qquad (3)$$

The modified formula uses the model of nonlocal thermoelastic peak (NTP) for calculation of the number of thermoactivated transitions $w(E,u,T_0)$ produced by low-energy ion:

$$w(E,u,T_0) = n_0 \nu \int_0^{\tau_c} V(t,E) e^{-\frac{u}{k_B T(t,E,T_0)}}\, dt, \qquad (4)$$

where k_B is the Boltzmann constant, n_0 is the atomic concentration, ν is the frequency of atomic oscillations, T_0 is the substrate temperature, T is the temperature in NTP, $V(t, E)$ is the NTP volume, and τ_c is the life time of the NTP: $\tau_c \sim R_{NTP}^2/(4\kappa)$, where R_{NTP} is the radius of the NTP, and κ is the thermal diffusivity [3]. At calculation the life time τ_c is chosen on the basis of analysis of behavior of integrand depending on E and u values.

The modified formula permitted explaining a set of regularities observing at deposition of carbon and BN coatings. The typical feature of these two cases is that deposited ions are the single charged ones. At the same time, the use of pulse potential mode for deposition of differently charged Ti^+, Mo^+ and other ions requires generalization of the theory of intrinsic stress in the coating.

The goal of the work is to derive the formula for calculation of intrinsic stress in coatings deposited in the pulse potential mode, taking into account differently charged ions.

2. MATHEMATICAL MODEL

Deriving formula for intrinsic stress we followed the reasoning used by C.A. Davis [1]. Intrinsic stresses arise as a result of two opposite processes: 1) subsurface ion implantation, leading to the emergence of volumetric strain and compressive stress, and 2) decrease

of defect number due to their thermal migration in ion NTPs and drain to boundaries. The last leads to stress relaxation.

In the pulse potential mode ions of two different energies $E_0 + ie(U+U_0)$ and $E_0 + ieU_0$ are alternately deposited. Here E_0 is the initial ion energy, U is the potential supplied to the substrate, U_0 is the floating potential, e is the proton charge, and i is the charge of the ion in units of the proton charge. If the duration and the repetition frequency of high-energy pulses are equal to t_p and f, respectively, then the duration of the period when the target is irradiated with low-energy ions is equal to $f^{-1} - t_p$ where $f^{-1} > t_p$. In this case, the intrinsic compressive stresses which are established in the coating depend on the type of the coating occurring. Thus, if the pulse width is sufficiently large, then material which is deposited during each pulse can be regarded as a solid layer of macroscopic thickness. The intrinsic stress in each layer should be evaluated using the expression (3), where E is the energy of the ions forming the concerned layer. In this case, the coating can be regarded as multi-layer sandwich, and the equilibrium stress can be calculated taking into account the stress and the thickness of each layer [4]. However, if the effective thickness of each layer does not exceed the interatomic distance a, it is senseless to talk about the stress formation in each of these 'layers', because the size of the ion NTP is considerably higher than the layer thickness [2]. In this case, we can assume that the coating is formed by a mixture of ions of two different energies (approximation of mixed beam), and the proportion of ions with energies $E_0 + ie(U+U_0)$ and $E_0 + ieU_0$ is ft_p and $1 - ft_p$, accordingly. Condition for the realization of the last case has the form:

$$t_p \le \frac{1}{Ra^2}, \qquad (5)$$

Taking for estimations R= 5 mA/cm^2 = $3 \cdot 10^{16}$ cm^{-2}s^{-1}, a =$2.5 \cdot 10^{-8}$ cm, we get from (5): $t_p \le 0.05$ s. In the pulse potential mode they use pulses with t_p from 10 to 30 μs, so you can use the mixed beam approximation to describe intrinsic stress generation.

The proposed model, as well as the Davis model [1] is based on the hypothesis of a linear relation between volumetric deformation of solid films bombarded by energetic particles, and density of defects formed as a result of scattering of primary ions and recoils on the target atoms.

As was supposed in [5], the rate of formation of defects per unit area $\dot{n}_i$ is associated with the flux density of bombarding ions j and with ion energy E by ratio $\dot{n}_i \sim jE^{1/2}$. We use some different function for $\dot{n}_i$. It is given by a direct calculation using code SRIM2000 of the relative part $\upsilon(E)$ of ion energy E used to produce defects. In accordance with definition of function $\upsilon(E)$, the expression for the rate of defect formation can be represented as:

$$\dot{n}_i \sim j\left[E\,\upsilon(E)/E_d + \Upsilon\right] \qquad ,(6)$$

where Υ is the own contribution of the primary ion in the volumetric strain due to its implantation, E_d is the displacement energy for TiN. In the calculation we assumed $E_d = 25$ eV.

If ions of two different energies are present in the flux, then equation (6) can be rewritten as:

$$\dot{n}_i \sim j\left[ft_p\zeta\left(ie(U+U_0)+E_0\right)+(1-ft_p)\zeta\left(ieU_0+E_0\right)\right], \qquad (7)$$

where designation $\zeta(E) = \left(E\upsilon(E)/E_d + \Upsilon\right)$ is introduced.

Stress relaxation is determined by the number of thermally activated transitions of atoms in the ion NTP according to expression (4). The relaxation rate $\dot{n}_R$ per unit area is proportional to the number of thermally activated transitions of atoms in the ion NTP $w(E,u,T_0)$, to fraction of atoms which are in metastable states n/n_0, and to the flux of implanted ions j:

$$\dot{n}_R = \frac{n}{n_0} jw(E,u,T_0), \qquad (8)$$

where n is the defect concentration.

If the ion flux consists of ions of two different energies they produce NTPs of two different types, depositing various contributions to production of thermally activated transitions. With this in mind, the expression for $\dot{n}_R$ takes the form:

$$\dot{n}_R = \frac{n}{n_0} j\left[ft_p w\left(ie(U+U_0)+E_0\right)+(1-ft_p)w\left(ieU_0+E_0\right)\right]. \qquad (9)$$

Here and below we omit dependence of w function on parameters u and T_0.

Stress in the coating can be calculated based on the assumption that there is balance between processes of defects generation by ion implantation and their loss due to migration.

The rate per unit area at which the defects are introduced into the film, is equal to $R(n/n_0)$, where R is the total rate per unit area of attachment of atoms to a growing film. On the other hand, the resultant rate of introducing defects given by the difference between the rate of defect generation due to ion implantation and the rate of their loss due to thermally activated migration. Consequently, the condition of stationarity (i.e., constancy of defect density) leads to the relation [1]:

$$\dot{n}_i = R\frac{n}{n_0} + \dot{n}_R. \qquad (10)$$

Substituting $\dot{n}_i$ and $\dot{n}_R$ in (10) and expressing the proportion n/n_0 of the ions implanted in the film from obtained equation, we get:

$$\frac{n}{n_0} \sim \frac{ft_p\zeta\left(ie(U+U_0)+E_0\right)+(1-ft_p)\zeta\left(ieU_0+E_0\right)}{\xi + ft_p w\left(ie(U+U_0)+E_0\right)+(1-ft_p)w\left(ieU_0+E_0\right)} \qquad (11)$$

According assumption, the volumetric strain υ is proportional to the fraction of implanted atoms n/n0 in the film. In a case of thin coatings we have the next expression for compressive stress acting in the plane of

the coating $\sigma = E_Y \upsilon/(1-\Pi)$. The result is:

$$\sigma(U) \sim \frac{E_Y}{1-\Pi} \times \times \frac{ft_p \zeta\left(ie(U+U_0)+E_0\right)+(1-ft_p)\zeta(ieU_0+E_0)}{\xi+ft_p w\left(ie(U+U_0)+E_0\right)+(1-ft_p)w(ieU_0+E_0)}, \quad (12)$$

If ion flux contains ions of different charge states,

$$\sigma(U) \sim \frac{E_Y}{1-\Pi} \frac{ft_p \sum_i \chi_i \zeta\left(ie(U+U_0)+E_0\right)+(1-ft_p)\sum_i \chi_i \zeta(ieU_0+E_0)}{\xi+ft_p \sum_i \chi_i w\left(ie(U+U_0)+E_0\right)+(1-ft_p)\sum_i \chi_i w(ieU_0+E_0)}. \quad (13)$$

Here χ_i is the relative part of ions with charge equal to ie, and $\sum_i \chi_i = 1$. Assuming $ft_p = 1$ we obtain expression for intrinsic stress in the case of the DC mode:

$$\sigma(U) \sim \frac{E_Y}{1-\Pi} \frac{\sum_i^z \chi_i \zeta\left(ie(U+U_0)+E_0\right)}{\xi+\sum_i^z \chi_i w\left(ie(U+U_0)+E_0, u, T_0\right)}. \quad (14)$$

In the case of singly charged ion flux $\chi_i = \delta_{i1}$ and equation (14) is transformed into known expression (3).

3. CALCULATION RESULTS AND DISCUSSION

To calculate intrinsic stress in the TiN coating at ions Ti implantation, we used formula (13) where were taken ft_p = 0.12 and ft_p = 1 for modes of pulse and constant potential, respectively. According to the data presented in [6], the ions Ti have charge from 1 to 3, at that χ_1 = 0.27; χ_2 = 0.67; χ_3 = 0.06.

When calculating the intrinsic stresses in the deposited coating, it is necessary to consider the deposition temperature T_0 which can significantly vary with ion energy because the ion flux heats the surface of the coating. One can show that in approximation of the linear heat equation with constant thermal conductivity in steady state deposition temperature T_0 is associated with potential U by linear dependence $T_0(U) = \lambda\left[\bar{q}(U+U_0)+E_0\right]+T_{00}$ where $\bar{q} = e\sum_i i\chi_i$ is the average ion charge (in considered case $\bar{q} = 1.79e$), T_{00} is the temperature of unexposed substrate. Value λ depends on the technical parameters of the installation for coating deposition. In this study, it is chosen from the condition that the deposition temperature is equal to its experimental value at certain energy of deposited ions. In accordance with data given in [7], $T(U = 0\ \text{V})$ = 573 K and $T(U = 540\ \text{V})$ = 873 K, that gives an estimate λ = 0.3 K/eV.

Fig. 1 shows the dependence of intrinsic stress on the substrate potential U in the coating TiN, deposited in the DC mode (curve 1) with parameters u = 0.59 eV, U_0 = 20 V, E_0 = 40 eV, λ = 0.3 K/eV, $T(0\ \text{V})$ = 573 K.

Maximum stress σ_m = 6.6 GPa achieved at a potential U = 50 V. The black circles correspond to values obtained in the experiment [7]. The dashed curve corresponds to stress in the coating deposited at lower temperature $T(0\ \text{V})$ = 473 K. As can be seen from the figure, reducing of the deposition temperature leads to significant increase in stress.

they will also gain different energy in the accelerating potential U and, therefore, are characterized by different abilities of defect generation and different rates of defect migration. Arguments similar to those at derivation of equation (12) lead to the following expression for intrinsic stress in the coating deposited from differently charged ions in the pulse potential mode:

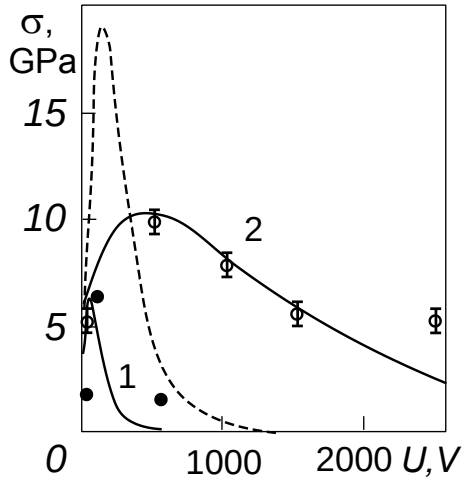

Fig. 1. Dependence of intrinsic stress in the coating TiN deposited in DC (curve 1) and pulse potential (curve 2) modes on the substrate potential U.

Curve 2 corresponds to intrinsic stress in the coating TiN, deposited in the pulse potential mode with the following parameters: u = 0.59 eV, f = 24 kHz, t_p = 5 μs, U_0 = 20 V, E_0 = 40 eV, $T(0\ \text{V})$ = 473 K. The maximum stress σ_m = 10.2 GPa achieved at substrate potential U = 430 V. The open circles marked stress values obtained in the experiment [8]. The theoretical curves are normalized to the maximum value of stress obtained in the experiment in the pulsed potential mode.

As can be seen from fig 1, there is qualitative agreement between theoretical curves and experimental data. Particularly, maximum of $\sigma(U)$ in the pulse potential mode shifts considerably in the range of higher ion energies compared with the case of DC mode, in accordance with experiments [7,8]. Observed discrepancy can be explained by inaccurate choice when calculating the values of the average charge $\bar{q}$ and initial energy E, compared with the real values. In addition, better agreement between calculated values of σ and experimental data can be achieved by making small changes in the geometric parameters of the NTP. However, this goal was not intended in this study. Importantly, the deposition in the pulse potential mode results in a significantly lower intrinsic stress than in the case of the DC mode at the same temperature.

4. CONCLUSIONS

1. Within the model of nonlocal thermoelastic peak of low-energy ion the expression for intrinsic stress in coating deposited in plasma environment with simultaneous bombardment ion flux was obtained. The expression accounts for the presence of ions of different charges and is valid in the modes both DC and pulsed potential.

2. Comparison of calculation results of intrinsic stress in TiN coatings deposited from the Ti ion beam with experimental data shows their qualitative agreement. Deposition in the pulsed potential mode leads to significantly less stress than deposition in the DC mode at the same temperature. Pulse mode allows to produce coatings with low intrinsic stress at relatively low deposition temperatures which eliminates the chemical decomposition and/or phase separation in the deposited coating.

REFERENCES

1. C.A. Davis, *Thin Solid Films* **226**, 30 (1993).
2. A.I. Kalinichenko, S.S. Perepelkin, V.E. Strel'nitskij, *Problems of atomic science and technology, series: "Physics of radiation damages and radiation material science"* **No6**, 116 (2007). [In Russian]
3. A.I. Kalinichenko, S.S. Perepelkin, V.E. Strel'nitskij, *Diam. Relat. Mater.* **15**, 365 (2006).
4. A.I. Kalinichenko, V.V. Vasyliev, V.E. Strel'nitskij, *Proc. NAP* **1** No4, 04PITSE07 (2012).
5. H. Windischmann, *J. Appl. Phys.* **62**, 1800 (1987).
6. I.I. Aksenov, A.A. Andreev, V.A. Belous, et al. *Vacuum Arc: Plasma Sources, Coating Deposition, Surface Modification* (Naukova Dumka: Kyiv: 2012).
7. H. Ljungcrantz, L. Hultman, J.-E. Sundgren, L. Karlsson, *J. Appl. Phys*. **78**, 832 (1995).
8. S.S. Akkaya, V.V. Vasyliev, E.N. Reshetnyak, K. Kazmanli, N. Solak, V.E. Strel'nitskij, M. Ürgen, *Surf. Coat. Tech*. **236**, 332 (2013).